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PRODUCTION OF WHITE PIGMENTS BASED ON ZIRCONATES AND TITANATES USING THE PRECIPITATION METHOD

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Experimental data on the synthesis of zirconates and titanates of *s* and *d* elements of group II by the precipitation method are summarized. It is established that a chemical reaction takes place between the components under alkaline precipitation. Subsequent thermal treatment of the obtained precipitate makes it possible to synthesize materials with a perovskite-like structure, which are recommended as white pigments for producing paints suitable for decorating glass and enamel articles.

The present study continues our systematic research dedicated to producing pigments of the perovskite-like structure using the method of precipitation from aqueous salt solutions [1–6]. The studies performed have demonstrated the fundamental possibility of synthesizing pigments with good chromophore properties by heat treatment of precipitated titanates and zirconates of bivalent metals. Most of these studies were focused on tinted and not on white pigments, which are mainly used in decorating glass articles and producing white enamels.

The present study describes the results of an experiment in synthesizing precipitates which after heat treatment yield white pigments of the perovskite-like structure based on the systems $\text{CaO} - \text{TiO}_2$, $\text{SrO} - \text{TiO}_2$, $\text{CdO} - \text{TiO}_2$, $\text{SrO} - \text{ZrO}_2$, $\text{ZnO} - \text{ZrO}_2$, $\text{CdO} - \text{ZrO}_2$, and $\text{ZrO}_2 - \text{TiO}_2$ with a high whiteness index. The synthesis and study of white pigments using the methods of differential thermal analysis, x-ray phase analysis, and IR-spectroscopy were performed in the same way as in our previous studies. The kinetic parameters and the activation energy of thermal decomposition of samples in the $\text{ZnO} - \text{ZrO}_2$ system were determined for the first time.

The initial materials were CaCl_2 (“pure”), $\text{Sr}(\text{NO}_3)_2$ (“analytical grade”), CdSO_4 (“analytical grade”), $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ (“chemically pure”), $\text{Ti}(\text{SO}_4)_2$ (pure), TiO_2 (“pure”), $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (“chemically pure”), and ZrO_2 (“pure”). To obtain zirconates and titanates, we prepared aqueous solutions of salts with a concentration of 0.5 M and mixed them in a ratio of $\text{MeO} : \text{Zr}(\text{Ti})\text{O}_2 = 1 : 1$, where Me is Ca, Sr, Zn, or Cd. Precipitation was carried out using 1 M solution of NaOH (“pure”). The optimum quantity of the precipitator was determined based on pH-titration data [4].

Based on pH-titration curves, it was established that alkaline coprecipitation of ions in the systems $\text{Me}(\text{II}) - \text{Ti}(\text{IV})$ and $\text{Me}(\text{II}) - \text{Zr}(\text{IV})$, as well as heterophase alkaline precipitation of $\text{Me}(\text{II})$ ions in the presence of solid TiO_2 and ZrO_2 produce precipitates of $\text{Me}(\text{II})$ titanates and zirconates [2–6]. The curve of the titration of $\text{Zr}(\text{IV}) - \text{Ti}(\text{IV})$ solution by alkali exhibits a single jump (Fig. 1). At the same time, judging by the products of the solubilities of the hydroxides that are equal to 7.9×10^{-55} and 6.3×10^{-52} for $\text{Zr}(\text{OH})_4$ and $\text{Ti}(\text{OH})_4$, respectively [7], the curve should have two jumps corresponding to the consecutive precipitation of two hydroxides; however, such a result has not been observed. Consequently, a chemical reaction between the components occurs in the $\text{Zr}(\text{IV}) - \text{Ti}(\text{IV})$ system under alkaline precipitation as well.

The resulting precipitates after their rinsing, filtering, and drying were studied by the DTA method (Paulik – Paulik – Erdey derivatograph, heating rate 10 K/min). We have earlier demonstrated that substitutional solid solutions

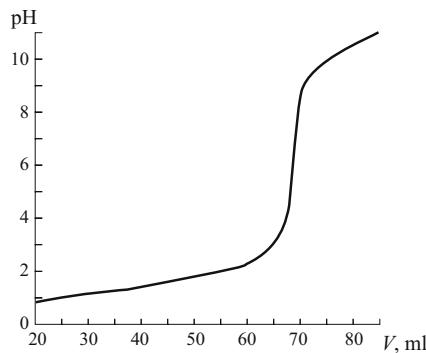


Fig. 1. Curve of pH titration of $\text{Zr}(\text{IV}) - \text{Ti}(\text{IV})$ solution.

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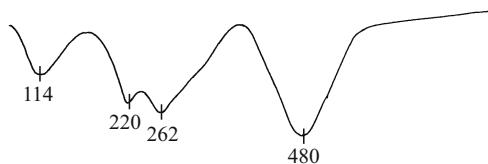


Fig. 2. Thermogram (°C) of hydroxide precipitate of Cd(II) – Ti(IV).

of hydroxides are formed in the systems $\text{SrO} - \text{ZrO}_2$ and $\text{CdO} - \text{ZrO}_2$ [4]. The DTA curve of the sample $\text{CdO} \cdot \text{TiO} \cdot n\text{H}_2\text{O}$ (Fig. 2) points to its stepwise dehydration (the endothermic effects at temperatures of 114, 220, 262, and 480°C). Since precipitation proceeds in the presence of solid TiO_2 , all the effects observed may be related either to $\text{CdO} \cdot n\text{H}_2\text{O}$, or to a new compound. It is known [8] that cadmium (II) hydroxide decomposes at a temperature above 170°C. Consequently, the clearly defined endothermic effects presumably belong to cadmium (II) titanate that is formed in precipitation. Considering the significant difference in the acid-base properties of Cd(II) and Ti(IV) aquions [4, 7], it is reasonable to assume the probability of formation of such a compound.

We have also carried out experiments to determine the weight losses of the synthesized samples upon their isothermal exposure in air at a temperature of 1000°C for 1 h (Table 1). Furthermore, Table 1 shows the estimated weight losses calculated using the additivity rule for a mechanical mixture of hydroxides taken in the molar ratio of 1 : 1. Since

the experimentally determined content of water in the $\text{Cd(II)} - \text{TiO}_2$ system is significantly lower than the quantity calculated using the additivity rule, we can assume the formation of a chemical compound in this system [9]. In contrast, the amount of water in the $\text{Zn(II)} - \text{ZrO}_2$ system is larger than the calculated amount; consequently, in this case a substitutional solid solution of hydroxides has been formed [9]. In the system $\text{Cd(II)} - \text{ZrO}_2$, the experimental and estimated quantities of water virtually coincide within the limits of experimental error.

To determine the kinetic parameters of the process of thermal decomposition of samples in nonisothermal conditions, we have used the approach described in [10]. The thermogravimetric data are obtained on the same derivatograph in the interval from room temperature to 1000°C for different heating rates (2.5, 5.0, 10.0, and 20.0 K/min). The experiments were conducted in air in open ceramic crucibles. The weight of powdered samples was around 1 g. The reference standard was calcined alumina. The kinetic parameters of the thermal decomposition of samples (Table 2) were calculated on a computer using the KINTOOL special program. The degree of transformation α was accepted as the ratio of the experimental weight loss of a corresponding sample by the moment of reaching a particular temperature (under a constant heating rate) to the weight loss of the same sample obtained in additional experiments (under isothermal exposure in air at 1000°C for 1 h). The obtained data show that the decomposition of the sample produced in the system $\text{ZnO} - \text{ZrO}_2$ is more complex than the decomposition of other studied samples.

After the synthesized precipitates were heat-treated at 1000°C for 1 h, they were studied by the IR spectroscopy method. In the spectrum of the sample produced in the calcination of zirconium hydroxide the position of all absorption bands corresponds to the set of absorption frequencies of the monoclinic modification of ZrO_2 described in the literature [11] (260, 350, 410, 450, 520, 575, 630 — an arm, 735 cm^{-1}). The absorption spectrum of the sample synthesized in the heat treatment of coprecipitated cadmium and zirconium hydroxides has absorption bands at frequencies of 80, 165, 220, 255, 325, 380, 415, 420, 430, 450, 512, 538, 560, 580, 616, and 756 cm^{-1} . It follows from these data that

the spectrum of the sample of the $\text{CdO} - \text{ZrO}_2$ system has virtually no absorption bands typical of ZrO_2 , but has intense bands with other frequency values in the vibration range of the Me – O bond, which points to the formation of cadmium zirconate. Since some low-intensity absorption bands (255, 415, 450, 580 cm^{-1}) are close to the frequencies of the ZrO_2 absorption bands, we can also assume the presence of a ZrO_2 impurity in the sample.

The absorption spectrum of the sample obtained by the precipitation of $\text{CdO} \cdot n\text{H}_2\text{O}$

TABLE 1

Sample composition	Weight losses, %	
	experimental	estimated
TiO_2	0.17	—
$\text{ZrO}_2 \cdot n\text{H}_2\text{O}$	29.97	—
$\text{ZnO} \cdot n\text{H}_2\text{O}$	26.68	—
$\text{CdO} \cdot n\text{H}_2\text{O}$	26.65	—
$\text{CdO} \cdot \text{TiO}_2 \cdot n\text{H}_2\text{O}$	12.11	26.74
$\text{ZnO} \cdot \text{ZrO}_2 \cdot n\text{H}_2\text{O}$	32.57	28.33
$\text{CdO} \cdot \text{ZrO}_2 \cdot n\text{H}_2\text{O}$	27.21	28.31

TABLE 2

Sample composition	Degree of transformation	Optimum kinetic model	Activation energy, kJ/mole
$\text{ZrO}_2 \cdot n\text{H}_2\text{O}$	$0.05 < \alpha < 0.35$	First-order equation	Monotonic increase from 40 to 70
	$0.35 < \alpha < 0.60$		65 – 70
$\text{CdO} \cdot n\text{H}_2\text{O}$	$\alpha > 0.40$	Equation of compressing volume (sphere)	120 – 140
	$0 < \alpha < 0.20$	The same	70 – 75
$\text{ZnO} \cdot \text{ZrO}_2 \cdot n\text{H}_2\text{O}$	$0.20 < \alpha < 0.40$	Equation of compressing area (cylinder)	Monotonic decrease from 95 to 86
	$0.40 < \alpha < 0.60$	First-order equation	65 – 70

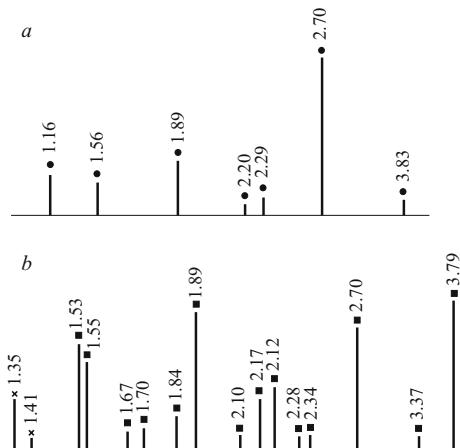


Fig. 3. X-ray diffraction patterns of calcined samples (\AA) of systems $\text{CaO} - \text{TiO}_2$ (a) and $\text{CdO} - \text{TiO}_2$ (b): ● CaTiO_3 ; ■ CdTiO_3 ; x CdO .

in the presence of solid TiO_2 and its subsequent calcination has the following frequency sets (cm^{-1}): 320, 355 (an arm), 420, 435, 540, 556, 696 (an arm), 700 (an arm), 1090, 1170 (an arm). The position of the absorption bands at 320, 420, and 435 cm^{-1} virtually coincides with the position of absorption bands in the spectrum of the $\text{CdO} - \text{ZrO}_2$ sample. This gives grounds to attribute these bands to the vibrations of the $\text{Cd} - \text{O}$ bond in both samples (systems $\text{CdO} - \text{ZrO}_2$ and $\text{CdO} - \text{TiO}_2$).

The calcined sample of the $\text{SrO} - \text{TiO}_2$ system has a simple spectrum with absorption bands at 530, 600, and $1080 - 1094 \text{ cm}^{-1}$. The latter band is common for the spectra of $\text{SrO} - \text{TiO}_2$ and $\text{CdO} - \text{TiO}_2$, which gives grounds to attribute it to the vibrations of the $\text{Ti} - \text{O}$ link in these titanates.

After the thermal treatment of the synthesized precipitates at 1200°C for 1 h they were studied by x-ray phase analysis on a DRON-3 diffractometer with ionization registration of scattered rays (CuK_α radiation, 1000 pulses/sec, a Geiger counter). The diffraction patterns were decoded using the JCPDS x-ray diffraction database (USA). In our study [4] using the x-ray phase analysis method we established that two phases (a zirconate and MeO) are formed in the systems $\text{SrO} - \text{ZrO}_2$ and $\text{CdO} - \text{ZrO}_2$, where a slight excess of MeO stabilizes the crystal lattice of ZrO_2 . In both cases the formation of substitutional solid solutions is registered. The x-ray phase analysis of the calcined samples obtained in the $\text{CaO} - \text{TiO}_2$ and $\text{CdO} - \text{TiO}_2$ systems identified the reflection belonging to calcium and cadmium titanates in both diffraction patterns (Fig. 3). Furthermore, a small quantity of the CdO phase persists in the $\text{CdO} - \text{TiO}_2$ system.

Thus, we have established the formation of titanates and zirconates for a number of elements of group II upon coprecipitation of hydroxides or precipitation of $\text{MeO} \cdot n\text{H}_2\text{O}$ hydroxides in the presence of solid ZrO_2 and TiO_2 , as well as upon subsequent heat treatment of the obtained precipitates.

TABLE 3

Pigment composition	Weight content, %	Whiteness, %
$\text{CaO} \cdot \text{TiO}_2$	5	35
$\text{CdO} \cdot \text{TiO}_2$	5	52
$\text{CaO} \cdot \text{ZrO}_2$	5	56
$\text{SrO} \cdot \text{ZrO}_2$	5	76
$\text{ZnO} \cdot \text{ZrO}_2$	5	38
	10	55
	15	31
$\text{CdO} \cdot \text{ZrO}_2$	5	51
	10	37
	15	39
$\text{ZrO}_2 \cdot \text{TiO}_2$	5	46

This provides the basis for the synthesis of stable white pigments with a perovskite-like structure.

The calcined precipitates were mixed with low-melting fluxes to obtain ceramic paints. They were thoroughly rubbed to powder, deposited on a glass substrate, and fixed at a temperature of $600 \pm 5^\circ\text{C}$. After that their whiteness was measured with a luster meter (Table 3). The flux : pigment ratio varied from 95 : 5 to 85 : 15.

The pigment content being equal (5%), the maximum whiteness (over 50%) is registered in paints based on the $\text{CaO} - \text{ZrO}_2$, $\text{CdO} - \text{TiO}_2$, and $\text{CdO} - \text{ZrO}_2$ systems, and the paint based on the $\text{SrO} - \text{ZrO}_2$ system has whiteness equal to 76%. The variation in whiteness depending on the flux : pigment ratio differs for the systems $\text{ZnO} - \text{ZrO}_2$ and $\text{CdO} - \text{ZrO}_2$. In the former case, as the pigment content grows to 10%, the whiteness reaches its maximum (55%) and then abruptly decreases; in the latter case the maximum whiteness is observed with the minimal pigment content (5%).

The synthesized white pigments with the perovskite-like structure have a refractive index over 2.2; therefore, they can be used as opacifying phases in producing white paints for glasses and enamels. The proposed pigments improve the whiteness, luster, and resistance of decorated glasses and enamels to the impact of different reactants. Furthermore, their synthesis is performed at a temperature lower by $50 - 100^\circ\text{C}$ than the synthesis of pigments produced by the traditional powder technology.

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